

COMPOSITION FOR HARD ARTICLE SURFACE CLEANING LIQUID

FIELD OF THE INVENTION

The present invention relates to a fragrant
5 composition for a hard article surface cleaning liquid and
an acidic hard article surface cleaning liquid composition
containing the fragrant composition, the cleaning liquid
composition being adjusted so as to be acidic with an
organic acid. Particularly, it relates to a fragrant
10 composition for a hard article surface cleaning liquid and
a hard article surface cleaning liquid composition adjusted
to pH 2.0 to 3.0 with an organic acid.

BACKGROUND OF THE INVENTION

Heretofore, a large number of cleaning agents
15 suitable for cleaning surface of hard articles such as
bathroom tiles and toilet seats in a house have been
developed and reported. Among these cleaning agents, in
view of cleaning efficiency and safety in use, hard article
surface cleaning agents acidified with an organic acid have
20 been attracted much attention. As technologies on the
cleaning agents, there are reported a combined use of an
organic acid and sodium salt of an organic acid (JP-A-53-
94309), a combined use of a hydroxy carboxylic acid and a
surfactant (JP-A-55-147600), solidification of constituents
25 of a hydroxy carboxylic acid etc. (JP-B-7-116479), and an
acidic microemulsion containing a hydroxy carboxylic acid

(JP-A-7-305100, EP 630963 A2). These technologies focuses on cleaning function how to remove stains and purposes to enhance cleaning power. Each of the publications contains a description of possible combined use of a fragrant material in the cleaning agent but no precise investigation has been made on the fragrant material to be used and detail of the fragrant material has not been described. JP-A-7-305100 only discloses that α -terpineol is suitable as the fragrant material but the compound is only described as suitable but is not investigated in detail, still less the other fragrant materials.

Recently, with regard to cleaning liquids, a product which has not only a high cleaning power but also is scented with fragrance pleasant to consumers has been required. In particular, for a product used in the house, it is strongly requested that a pleasant fragrance is maintained over a long period of time. However, the request cannot be satisfied even if a fragrant material be only added and mixed in the cleaning liquid for satisfying the request. The reason is mainly as follows. That is, many of fragrant materials are compounds having an ester group or an aldehyde group and in the case of a long-term storage of strongly acidic aqueous solution or dispersion of the fragrant materials, there is a possibility that the fragrant materials are hydrolyzed or oxidized during the storage. In particular, in the case of a long-term storage

of strongly acidic aqueous solution or dispersion containing the fragrant compounds, there is a risk of deterioration of initial quality, e.g., change in appearance of the solution or dispersion, deterioration of the fragrance, or formation of precipitates.

An aqueous solution or dispersion adjusted so as to be strongly acidic with an organic acid can be widely utilized as a hard article surface cleaning agent but it is extremely important to provide a product scented with a pleasant fragrance in use. At selection of a fragrant material to be mixed, a fragrant compound or fragrant composition stable in an acidic hard article surface cleaning liquid adjusted so as to be strongly acidic, particularly to pH 2.0 to 3.0 is required.

SUMMARY OF THE INVENTION

Accordingly, it is an object to find out a fragrant compound or fragrant composition stable for a long period of time in an acidic hard article surface cleaning liquid adjusted so as to be acidic, particularly to pH 2.0 to 3.0 with an organic acid. Furthermore, it is also an object to provide a hard article surface cleaning liquid composition which contains the fragrant compound or fragrant composition and is adjusted so as to be strongly acidic with an organic acid.

As a result of extensive studies for solving the above problems, a fragrant composition for cleaning liquid

for hard article surface, comprising one or more of
fragrant compounds selected from the group consisting of
2,6-dimethyl-2-heptanol, 3,3-dimethylcyclohexyl methyl
ketone, o-tert-butylcyclohexanol, α -amylcinnamic aldehyde,
5 α -damascone, γ -octalactone, γ -nonalactone, γ -decalactone,
anethole, ethyl benzoate, ethyl 2,2,6-
trimethylcyclohexanecarboxylate, 2,2,6-trimethyl-1-
crotonylcyclohexane, 6-acetyl-1,1,2,4,4,7-
hexamethyltetrahydronaphthalene, isoamyl phenylethyl ether,
10 methyl octin carbonate, 6,7-dihydro-1,1,2,3,3-pentamethyl-
4(5H)-indanone, tricyclodecenyl acetate, undecyl aldehyde,
fenchyl acetate, dihydrojasnone, cedryl methyl ether, p-
cresol, hexyl aldehyde, and rosephenone is a fragrant
composition which exhibit no change in appearance and
15 fragrant quality such as coloring and generation of
precipitates in the hard article surface cleaning liquid
adjusted so as to be acidic with an organic acid and
further hardly occurs change in pH of the hard article
surface cleaning liquid after a long-term storage as
20 compared with the initial composition.

Namely, the invention provides:

(1) a hard article surface cleaning liquid
composition, which comprises:

(a) a fragrant composition comprising one or more
25 of fragrant compounds selected from the group consisting of
2,6-dimethyl-2-heptanol, 3,3-dimethylcyclohexyl methyl

ketone, o-tert-butylcyclohexanol, α -amylcinnamic aldehyde,
 α -damascone, γ -octalactone, γ -nonalactone, γ -decalactone,
anethole, ethyl benzoate, ethyl 2,2,6-
trimethylcyclohexanecarboxylate, 2,2,6-trimethyl-1-
5 crotonylcyclohexane, 6-acetyl-1,1,2,4,4,7-
hexamethyltetrahydronaphthalene, isoamyl phenylethyl ether,
methyl octin carbonate, 6,7-dihydro-1,1,2,3,3-pentamethyl-
4(5H)-indanone, tricyclodecenyl acetate, undecyl aldehyde,
fenchyl acetate, dihydrojasnone, cedryl methyl ether, p-
10 cresol, hexyl aldehyde, and rosephenone,
(b) an organic acid, and
(c) a surfactant;
(2) the above hard article surface cleaning liquid
composition, wherein the organic acid is oxalic acid and/or
15 malonic acid;
(3) the above hard article surface cleaning liquid
composition, wherein the organic acid is a hydroxy
carboxylic acid;
(4) the above hard article surface cleaning liquid
20 composition, wherein the hydroxy carboxylic acid is at
least one hydroxy carboxylic acid selected from the group
consisting of malic acid, citric acid, tartaric acid,
lactic acid, and gluconic acid;
(5) a hard article surface cleaning liquid
25 composition, which comprises:

(a) a fragrant composition comprising one or more of fragrant compounds selected from the group consisting of 2,6-dimethyl-2-heptanol, 3,3-dimethylcyclohexyl methyl ketone, o-tert-butylcyclohexanol, α -amylcinnamic aldehyde, α -damascone, γ -octalactone, γ -nonalactone, γ -decalactone, anethole, ethyl benzoate, ethyl 2,2,6-trimethylcyclohexanecarboxylate, 2,2,6-trimethyl-1-crotonylcyclohexane, 6-acetyl-1,1,2,4,4,7-hexamethyltetrahydronaphthalene, isoamyl phenylethyl ether, methyl octin carbonate, 6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone, tricyclodecenyl acetate, undecyl aldehyde, fenchyl acetate, dihydrojasnone, cedryl methyl ether, p-cresol, hexyl aldehyde, and rosephenone,

(b) an organic acid, and

(c) a surfactant, and

wherein the pH of the hard article surface cleaning liquid composition is within the range of from 2.0 to 3.0;

(6) the above hard article surface cleaning liquid composition, wherein the organic acid is oxalic acid and/or malonic acid;

(7) the above hard article surface cleaning liquid composition, wherein the organic acid is a hydroxy carboxylic acid; and

(8) the above hard article surface cleaning liquid composition, wherein the hydroxy carboxylic acid is at

least one hydroxy carboxylic acid selected from the group consisting of malic acid, citric acid, tartaric acid, lactic acid, and gluconic acid.

DETAILED DESCRIPTION OF THE INVENTION

5 The following will describe the invention in further detail.

 The fragrant compound for use in the invention includes 2,6-dimethyl-2-heptanol, 3,3-dimethylcyclohexyl methyl ketone, o-tert-butylcyclohexanol, α -amylcinnamic
10 aldehyde, α -damascone, γ -octalactone, γ -nonalactone, γ -decalactone, anethole, ethyl benzoate, ethyl 2,2,6-trimethylcyclohexanecarboxylate, 2,2,6-trimethyl-1-crotonylcyclohexane, 6-acetyl-1,1,2,4,4,7-hexamethyltetrahydronaphthalene, isoamyl phenylethyl ether,
15 methyl octin carbonate, 6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone, tricyclodecenyl acetate, undecyl aldehyde, fenchyl acetate, dihydrojasnone, cedryl methyl ether, p-cresol, hexyl aldehyde, and rosephenone. A fragrant composition for a hard article surface cleaning liquid is
20 prepared by mixing one or more compounds of these fragrant compounds. Moreover, in addition to the fragrant compounds, natural fragrant materials and essential oils containing these compounds can be used as fragrant constituents of the invention within a range capable of
25 achieving the aimed object. In this connection, the hard article means an article constituted by a substance itself

having a hard nature, which is used for bathtub or inner wall in a bathroom, toilet sheets in a lavatory, and sink or inner wall in a kitchen.

The above fragrant compounds can be synthesized by known methods. In addition, the above fragrant compounds or the natural fragrant materials and essential oils containing the compounds may be purchased as commercially available products.

In the invention, one or more fragrant compounds of the invention are mixed in an amount of 10% by weight to 100% by weight based on the total amount of the fragrant composition.

To the fragrant composition of the invention may be added the other fragrant compound or an additives, as far as the aimed object can be achieved. The above other fragrant compound may include allyl 2-pentyloxyglycolate, p-ethyl-2,2-dimethylhydrocinnamaldehyde, α -fenchyl alcohol, β -damascone, cis-3-hexenyl benzoate, 3a,6,6,9a-tetramethyldodecahydronaphtho[2,1-b]furan, isobornyl cyclohexanol, ethyl hexahydro-4,7-methanoindene-3a-carboxylate, coumarin, cumin aldehyde, amyl salicylate, benzyl salicylate, cyclamen aldehyde, allyl cyclohexylpropionate, dihydroindenyl-2,4-dioxane, methyl dihydrojasmonate, dihydromyrcenol, diphenyl oxide, cinnamic alcohol, tetrahydro muguol, ethyl phenylacetate, hexamethylhexahydrocyclopentabenzopyran, hexyl alcohol,

heptyl aldehyde, benzaldehyde, borneol, ethyl
methylphenylglycidate, menthone, raspberry ketone, and
undecyl aldehyde. Even when these fragrant compounds are
5 the mixture is stored for a long period of time, no change
is observed with time and also the fragrant quality changes
only a little, so that they can be used as suitable
fragrant compounds in the invention.

In the invention, a hard article surface cleaning
10 liquid composition adjusted so as to be strongly acidic can
be obtained by adding an organic acid to and mixing it with
the above fragrant composition. At that time, although a
more excellent cleaning effect is expectable at a lower pH
value, it is preferable to adjust the composition so as to
15 be acidic at about pH 2.0 to 3.0 in view of safety in
consideration of its use in a house.

As an organic acid for use in the invention,
oxalic acid and malonic acid are preferably used singly or
as a mixture thereof. As the other organic acid, hydroxy
20 carboxylic acids may be mentioned. Of these, at least one
hydroxy carboxylic acid selected from the group consisting
of malic acid, citric acid, tartaric acid, lactic acid, and
gluconic acid is particularly preferred.

It is preferable to add further a surfactant as a
25 solubilizing agent or emulsifying agent of the fragrant
material to the above hard article surface cleaning liquid

composition. As the above surfactant, there may be mentioned nonionic surfactants, for example.

Representative examples thereof include alcohol ethers and aliphatic acid alkanol amides containing a polyoxyethylene (average added moles of oxyethylene group being from 1 to 20) group and alcohol ethers and aliphatic acid alcohol amides containing a polyoxyethylene-polyoxypropylene (sum of average added moles of oxyethylene group and average added moles of oxypropylene group being from 1 to 20)

group. More specifically, examples thereof include polyoxyethylene(13) nonylphenyl ether, polyoxyethylene isostearyl ether, polyoxyethylene lauryl ether, polyoxyethylene oleylcetyl ether, polyoxyethylene stearyl ether, polyoxyethylene isocetyl ether, polyoxyethylene octyldodecyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene polyoxypropylene stearyl ether, polyoxyethylene polyoxypropylene cetyl ether, polyoxyethylene polyoxypropylene decyltetradecyl ether, polyoxyethylene polyoxypropylene butyl ether, polyoxyethylene polyoxypropylene behenyl ether, polyoxyethylene polyoxypropylene lauryl ether, polyoxypropylene lanolin alcohol ether, polyoxypropylene lanolin(S.P.O), polyoxypropylene myristyl ether, polyoxypropylene butyl ether, polyoxypropylene stearyl ether, polyoxypropylene cetyl ether, polyoxypropylene glyceryl ether, polyoxyethylene palm oil fattyacid

diethanolamide, and polyoxyethylene oleic acid diethanolamide.

In the invention, a thickening agent for adjusting the viscosity of the above composition and a coloring agent such as a dye or pigment for improving the appearance may be mixed. The above thickening agent includes polyacrylate salts, acrylic acid-maleic acid copolymers, and carboxymethyl cellulose derivatives. A small amount of an inorganic acid may be coexisted.

The hard article surface cleaning liquid composition thus prepared can be used as a final product of deodorant cleaning liquid even as it is but the other compounds which are mixed with a conventional hard article surface cleaning liquid may be further added and mixed.

Examples thereof include amphoteric surfactant-based deodorants, plant extracts, nonionic surfactants, anionic surfactants, and dyes.

The fragrant composition for a hard article surface cleaning liquid of the invention can be mixed with a hard article surface cleaning liquid composition. The amount thereof to be mixed is not particularly limited but the fragrant composition is preferably mixed in an amount of 0.01% by weight to 3.0% by weight, particularly 0.1% by weight to 0.5% by weight based on the total composition of the hard article surface cleaning liquid, for example.

The surfactant may be used in an amount of 1 to 20 times the weight of the fragrant composition. The amount of the organic acid is not particularly limited as long as the pH of the hard article surface cleaning liquid

5 composition can be adjusted within the range of from 2.0 to 3.0 and, for example, in an amount of 0.5 to 10% by weight based on the total composition of the hard article surface cleaning liquid composition.

The hard article surface cleaning liquid
10 composition or the product of the hard article surface cleaning liquid of the invention can be used especially for cleaning surface of hard articles such as tiles and bathtub in a bathroom and toilet seats in a lavatory.

The following will describe the invention
15 specifically with reference to Examples but the invention is by no means limited thereto.

Example 1

A hard article surface cleaning liquid composition was produced by mixing constituents of the following
20 formulation. The pH of the resulting composition was adjusted so as to be 2.0.

Constituent	% by weight
Malic acid (99.5%)	3.5
Polyoxyethylene(13) nonylphenyl ether	
5 (Nonipol 130)	3.0
Fragrant material	0.3
Purified water	balance
<hr/>	
Total	100.0

10 The fragrant material in the above formulation is each compound described in Table 1 and Table 2.

Example 2: Evaluation

15 In order to confirm the effect of the fragrant composition in the hard article surface cleaning liquid composition of the invention, the following evaluation was carried out. Specifically, sensory evaluation on appearance and fragrant quality of each composition was carried out by five panelists to judge the composition, and
20 presence of pH change was determined by means of a pH meter.

A 30 g portion of each solution of the hard article surface cleaning liquid compositions containing various fragrant compounds produced in Example 1 was placed
25 in each of two 50 ml glass vessel, followed by storage under a temperature of 50°C or 5°C (control). After

passage of 2 weeks or 4 weeks, sensory evaluation on appearance and fragrant quality of each hard article surface cleaning liquid composition stored at 50°C was carried out through comparison with the hard article surface cleaning liquid composition stored at 5°C. With regard to pH, a value after passage of 4 weeks at 5°C or 50°C was measured. In this connection, the pH of the cleaning liquid composition at the start of the experiment for evaluation was found to be 2.0. As a blank, using a hard article surface cleaning liquid composition produced without adding any fragrant material in the formulation of Example 1, sensory evaluation on appearance and fragrant quality was carried out and the pH value was measured as above. The results obtained are shown in Tables 1 and 2.

In this connection, it was confirmed that the hard article surface cleaning liquid composition containing a fragrant composition stored at 5°C was stable both in appearance and fragrant quality. Also, it was confirmed that the hard article surface cleaning liquid composition with no incorporation of any fragrant material, as a blank, did not change in appearance and fragrant quality and the pH changed only a little even after passage of 4 weeks.

The sensory evaluation on appearance and fragrant quality was carried out according to the following five ranks.

- 5: No change was observed.
- 4: A slight change was observed.
- 3: A change was observed.
- 2: A considerable change was observed.
- 5 1: A drastic change was observed.

Table 1

Name of fragrant compound	Sensory evaluation on appearance		Sensory evaluation on fragrant quality		5°C	50°C
	After 2 weeks	After 4 weeks	After 2 weeks	After 4 weeks	pH after 4 weeks	
2,6-Dimethyl-2-heptanol	5	5	5	5	1.94	1.94
3,3-Dimethylcyclohexyl methyl ketone	5	5	5	5	1.94	1.94
o-tert-Butylcyclohexanol	5	5	5	5	1.96	1.96
α -Amylcinnamic aldehyde	5	5	5	5	1.94	1.94
α -Damascone	5	5	5	5	1.95	1.95
γ -Octalactone	5	5	5	5	1.96	1.96
γ -Nonalactone	5	5	5	5	1.96	1.96
γ -Decalactone	5	5	5	5	1.94	1.94
Anethole	5	5	5	5	1.94	1.94
Ethyl benzoate	5	5	5	5	1.95	1.95
Ethyl 2,2,6-trimethylcyclohexanecarboxylate	5	5	5	5	1.94	1.94
2,2,6-Trimethyl-1-crotonylcyclohexane	5	5	5	5	1.94	1.94
6-acetyl-1,1,2,4,4,7-hexamethyltetrahydronaphthalene	5	5	5	5	1.94	1.94
Isoamyl phenylethyl ether	5	5	5	5	1.96	1.96
Methyl octin carbonate	5	5	5	5	1.96	1.96

Table 2: (continuation of Table 1)

Name of fragrant compound	Sensory evaluation on appearance		Sensory evaluation on fragrant quality		5°C	50°C
	After 2 weeks	After 4 weeks	After 2 weeks	After 4 weeks	pH after 4 weeks	
6,7-Dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone	5	5	5	5	1.94	1.94
Tricyclodecenyl acetate	5	5	5	5	1.95	1.95
Undecyl aldehyde	5	5	5	5	1.94	1.94
Fenchyl acetate	5	5	5	5	1.95	1.95
Dihydrojasmane	5	5	5	5	1.94	1.94
Cedryl methyl ether	5	5	5	5	1.95	1.95
p-Cresol	5	5	5	5	1.95	1.95
Hexyl aldehyde	5	5	5	5	1.94	1.94
Rosephenone	5	5	5	5	1.97	1.97

The compounds described in Tables 1 and 2

5 exhibited no change in appearance and fragrant quality, and also no change in pH was observed. Thus, the compounds were able to store in the hard article surface cleaning liquid composition at pH 2.0 for a long period of time.

Comparative Example

10 Using each fragrant compound described in Table 3, a hard article surface cleaning liquid composition was produced. Further, sensory evaluation and pH measurement were carried out in a similar manner to the case in Example 2.

15 The results obtained are shown in Table 3.

Table 3: Comparative Example

Name of fragrant compound	Sensory evaluation on appearance		Sensory evaluation on fragrant quality		5°C	50°C
	After 2 weeks	After 4 weeks	After 2 weeks	After 4 weeks	pH after 4 weeks	
Linalool	5	4 (yel- lowed)	1.5	1	1.96	1.95
Citronellol	5	5	3	3	1.95	1.95
Geraniol	4 (yel- lowed)	4 (yel- lowed)	2	1	1.96	1.96
Alloocimenol	5	5	1	1	1.96	1.96
Phenylethyl acetate	5	4.5	2	1	1.96	1.96
Terpineol	5	4.5	1	1	1.95	1.95
L-Menthol	5	5	4	3	1.96	1.96
Eucalyptus	5	5	5	3	1.95	1.95
Helional	4 (yel- lowed)	3 (yel- lowish browned)	4	4	1.94	1.94

When the fragrant compounds described in Table 3
 5 were stored in the acidic hard article surface cleaning
 liquid composition, changes with time that appearance was
 yellowed or fragrant quality was changed were observed.

According to the invention, there can be provided
 a fragrant compound and a fragrant composition capable of
 10 storage for a long period of time without changing the
 initial fragrant quality and appearance even under a
 strongly acidic condition, especially even when mixed with
 an acidic hard article cleaning liquid of pH 2.0 to 3.0.
 Furthermore, a hard article surface cleaning liquid
 15 composition containing the fragrant compound or fragrant

composition can be provided. The cleaning liquid composition is adjusted so as to be acidic with an organic acid and thus is excellent in safety and it also exhibits an excellent cleaning performance.

5 Furthermore, since the cleaning liquid product containing the fragrant compound or fragrant composition of the invention uses a stable fragrant material, the product exhibits no deterioration of the fragrant compound and thus can maintain a stable fragrance tone. Accordingly, the
10 product is extremely useful.

 While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing
15 from the scope thereof.

 This application is based on Japanese patent application No. 2002-235537 filed August 13, 2002, the entire contents thereof being hereby incorporated by
20 reference.